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Thermoanalytical study of selected transition bivalent metal complexes with 5-carbaldehyde-4-methylimidazole

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Bretsznajder Special Chapter

Abstract To compare thermal stability of Co(II), Zn(II), and Cd(II) complexes with 4-CHO-5-MeIm, the two compounds of formula $[MnL_2(NO_3)_2]$ and $[NiL_3](NO_3)_2$ have been prepared and structurally characterized. Elemental analysis and spectroscopic studies have confirmed a bidentate fashion of coordination of the ligand to Mn(II) and Ni(II) ions. IR and Raman spectra indicate that there are different coordination modes of the NO_3^- in compounds: non-coordinated and coordinated. The decomposition process of the studied complexes in nitrogen and argon (Ni(II) complex) atmosphere proceeds in three main stages, except Zn(II) complex, in temperature range 353–1163 K. The final products of decomposition are CoO, MnO, Cd, ZnN_4, NiN_3. In addition, we have to admit that the different coordination mode of the NO_3^- ions in complexes: non-coordinated (in the (**1**), (**4**), and (**5**)) and coordinated (in the (**2**) and (**3**)) correlate with its thermal behavior. Thus, temperature ranges of its decompositions are observed: below 533 K and above 533 K, respectively. In Co(II), Mn(II), and Cd(II) complexes the fragments of N-donor atom-containing ligands decompose in the last stages, contrary to Zn(II) and Ni(II) compounds, in which metal ion surrounded by N atoms remains until the end. The course of pyrolysis and molecular structure of the complexes lead to the same conclusion about the strength of metal–ligand bonds. On the basis of obtained results, it is concluded that the thermal stability of the studied compounds follows the order: (**1**) < (**5**) < (**2**) < (**3**) < (**4**).

Keywords Mn(II) · Co(II) · Cd(II) · Zn(II) and Ni(II) complexes · 4-methyl-5-carbaldehydeimidazole · IR and Raman spectra · TG/DTG analysis · Magnetic properties

Introduction

Complexes of 5-carbaldehyde-4-methylimidazole (5-CHO-4-MeIm, L) that contain transition metal ions have received attention from our research group over the past decade because of their interesting molecular and crystal architectures, and their potential application for models of zinc-metalloenzymes [1–11], copper-metalloenzymes [1, 12–16], catalytic oxidant of ROS [17–20], and for good chelating ability of toxic Cd(II) [1, 21–27] and Ni(II) ions [28–31].

4-CHO-5-MeIm is a molecule of considerable interest as a potential bidentate N,O-donor that can exist in two tautomeric forms: 5-CHO-4-MeIm (**1**) and 4-CHO-5-MeIm (**2**) (Scheme 1). Tautomeric equilibrium in the imidazole ring can lead to different modes of coordination of ligand toward metal ions. It is possible to predict that tautomer (**1**) can coordinate as a monodentate through N- or O-donors or as a bridging bidentate. Tautomer (**2**) allows the formation of five-membered chelate ring with central ion.

Our previous investigation [1, 22, 32] shows that revealed stabilization of tautomer (**2**) as the only one able to form a chelate ring with central atoms. Hence, we have studied the preference of the central ions to adopt a specific coordination number from 4 to 8 and the geometry of coordination polyhedra. We also analyzed the influence of the nature of the donor atoms and the function of the optionally monodentate or bidentate ligand by spectroscopic and structural methods. As the first crystal we obtained $[Cu(4\text{-CHO-5-MeIm})_4](NO_3)_2(H_2O)_2$ [32] (Scheme 2a) consists of four

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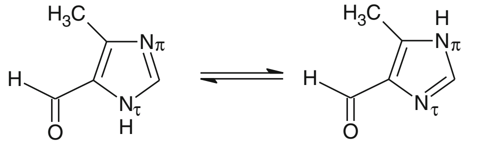
ligands which are bound to the Cu^{2+} ion in a bidentate fashion through the pyridine-like nitrogen atom of the imidazole ring and oxygen atom of the carbonyl group. The coordination polyhedron of this compound was described as distorted dodecahedron with CuN_4O_4 type of chromophore. The next example of eight-coordinated complex is $[Cd(4\text{-}CHO\text{-}5\text{-}MeIm)_2](NO_3)_2$ [1] (Scheme 2b). The heteroaromatic molecule acts as a N,O-donor ligand to give a CdN_2O_6 chromophore in which eight donor atoms participate, four from organic ligand and four from bidentate nitrate ions. The geometry of the coordination environment can be characterized as a double coordination sphere, the inner and external pseudo-tetrahedral symmetry. The other molar ratio M:L used in the same conditions of synthesis led to obtaining crystals of $[Cd(4\text{-}CHO\text{-}5\text{-}MeIm)_4](NO_3)_2(H_2O)$ [22] (Scheme 2c). In this case, coordination ability of ligand is the same as the above mentioned. The shape of the coordination sphere is a distorted dodecahedron of C_2 symmetry. In this polyhedron, oxygen atoms occupy the vertices with four neighbors and nitrogen atoms are in the vertices with five neighbors. In comparison to Cu(II) and Cd(II) complexes, $[Co(4\text{-}CHO\text{-}5\text{-}MeIm)_2(H_2O)_2](NO_3)_2$ [1] (Scheme 2d) has a geometry of distorted octahedral, with two symmetry-independent cations included in the unit cell. In both six-coordinate Co(II) complexes, two bidentate 4-CHO-5-MeIm species and two water molecules are coordinated to the central ion forming a CoN_2O_4 type of chromophore. $[Zn(4\text{-}CHO\text{-}5\text{-}MeIm)_4](NO_3)_2$ complex [1] (Scheme 2e) is quite different from all previous cited compounds in this study. In the coordination environment of the Zn^{2+} ion, there are four ligand moieties. Each molecule acts only as a monodentate nitrogen-donor ligand despite potential chelating ability of tautomer (**2**). The four identical Zn–N bond lengths and the values of N–Zn–N valence angles indicate that tetrahedral sphere is a good approximation for the Zn(II) ion.

In this article, we have been focused on the following studies:

(i) Presentation of the thermogravimetry (TG) and differential scanning calorimetry (DSC) of 4-CHO–5-MeIm complexes with Co(II), Mn(II), Cd(II), Zn(II), and Ni(II) ions;
(ii) Similarities and differences of thermal behavior of investigated series of 4-CHO–5-MeIm complexes;
(iii) Determination of final products of thermal decomposition processes;
(iv) Information on structural dependence of the thermal properties within examined transition metal complexes with 4-CHO-5-MeIm.



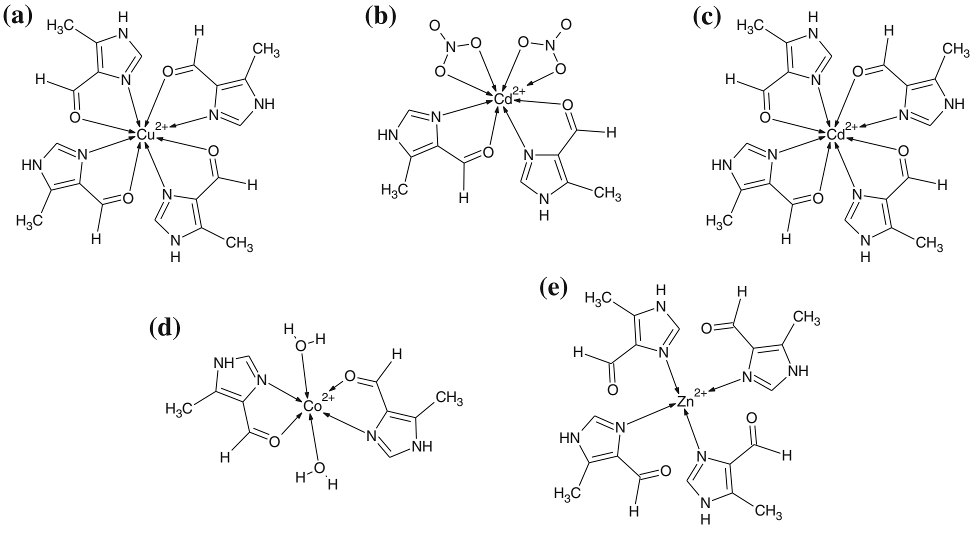
(1) (2)

Scheme 1 The tautomeric equilibrium between 5-CHO-4-MeIm (**1**) and 4-CHO-5-MeIm (**2**)

Experimental

Materials

$Co(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ were purchased from the Merck Chemical Company, 4-CHO-5-MeIm (Aldrich



Scheme 2 The coordination environments of $[Cu(4\text{-}CHO\text{-}5\text{-}MeIm)_4](NO_3)_2(H_2O)_2$ (**a**), $[Cd(4\text{-}CHO\text{-}5\text{-}MeIm)_2](NO_3)_2$ (**b**), $[Cd(4\text{-}CHO\text{-}5\text{-}MeIm)_4](NO_3)_2(H_2O)$ (**c**), $[Co(4\text{-}CHO\text{-}5\text{-}MeIm)_2(H_2O)_2](NO_3)_2$ (**d**), and $[Zn(4\text{-}CHO\text{-}5\text{-}MeIm)_4](NO_3)_2$ (**e**)

99.7%) and methanol, ethanol, *i*-PrOH (P.O.Ch. Gliwice) were used as received.

Methods

Chemical analysis

Elemental analysis was run on a Model Elemental Vario EL III CHN Analyzer.

XRD

The XRD investigations were carried out on a DRON-2 (Russia) diffractometer connected to an IBM computer, stepwise, over the 2θ angle range 5°–120°, using CuK_{α} radiation. The products of decomposition were studied using X-ray powder method.

Infrared (IR) and Raman analysis

IR spectra were recorded on Nicolet 380 FT-IR type spectrophotometer in the spectral range 4000–500 cm^{-1} using the ATR-diffusive reflection method. Fourier transform Raman scattering measurements (FT-RS) were performed at room temperature with a PerkinElemer RamanStation™ 400F spectrometer, resolution 4 cm^{-1}. The incident radiation ($\lambda = 785$ nm) came from a diode laser.

Thermal analysis

The thermal analyses (TG/DTG) were carried out using a TG/SDTA 851$^{\mathrm{e}}$ METTLER-TOLEDO thermobalance. The experiments were performed in argon and nitrogen atmosphere at a heating rate of 5 K min^{-1} in the temperature range 298–1273 K, using Al_2O_3 crucible. The sample sizes are ranged in mass from 1.65 to 5.46 mg. The thermoanalytical curves were obtained using STAR$^{\mathrm{e}}$ System METTLER-TOLEDO software. DSC analysis was carried out using DSC METTLER-TOLEDO Instrument in standard closed sample pans, static air atmosphere, and heating rate of 5 K min^{-1}.

Magnetic measurement

Magnetic measurements were carried out on a magnetic susceptibility balance (Sherwood Scientific) at room temperature by Gouy's method using $\mathrm{Hg[Co(NCS)_4]}$ as the calibrant.

Table 1 Elemental analysis data of Co(II), Mn(II), Cd(II), Zn(II), and Ni(II) complexes

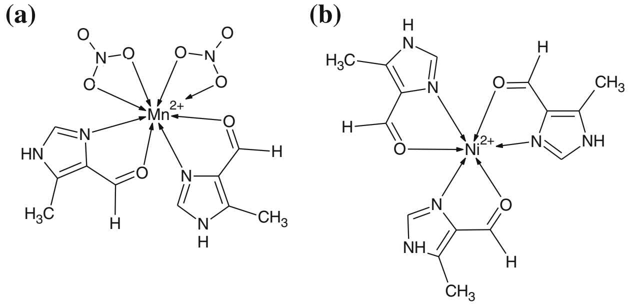
Complex	C/%		N/%		H/%	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\mathrm{[CoL_2(H_2O)_2](NO_3)_2}$ (**1**)	27.3	27.6	19.1	18.9	3.7	3.7
$\mathrm{[MnL_2(NO_3)_2]}$ (**2**)	30.0	30.3	21.0	21.1	3.2	3.5
$\mathrm{[CdL_2(NO_3)_2]}$ (**3**)	34.6	34.5	20.2	20.0	3.8	3.5
$\mathrm{[ZnL_4](NO_3)_2}$ (**4**)	45.8	45.4	22.2	22.1	3.2	3.0
$\mathrm{[NiL_3](NO_3)_2}$ (**5**)	38.5	38.7	22.5	22.4	3.9	3.9

Table 2 The characteristic IR (Raman) bands for complexes with 4-CHO-5-MeIm (L)/cm^{-1}

Assignment	L	Compounds				
		$\mathrm{[CoL_2(H_2O)_2](NO_3)_2}$ (**1**)	$\mathrm{[MnL_2(NO_3)_2]}$ (**2**)	$\mathrm{[CdL_2(NO_3)_2]}$ (**3**)	$\mathrm{[ZnL_4](NO_3)_2}$ (**4**)	$\mathrm{[NiL_3](NO_3)_2}$ (**5**)
ν(OH) H_2O	–	3409	–	–	–	–
ν(N–H)	3128 (3130)	3120 (3132)	3143 (3142)	3145 (3134)	3155 (3162)	3129
ν(C=O)	1665 (1662)	1612, 1585 (1611, 1582)	1659, 1635 (1662, 1640)	1660, 1635 (1634)	1665 (1668)	1605, 1574
ν(C=C)	1584 (1576)	1566 (1558)	1589 (1589)	1591 (1579)	1588 (1589)	1535
ν(C=N)	1455 (1458) 1439 (1440)	1464, 1440 (1452, 1441)	1476, 1453, 1434 (1472, 1450, 1438)	1464, 1456, 1436 (1460, 1447, 1421)	1467, 1456 (1469, 1455)	1458
Breath. ring vibrations	1158 (1159)	1145 (1150)	1146 (1148)	1150 (1144)	1171 (1172)	1155
ν NO_3^-	–	1365 (1366)	1401 (1400) 1757, 1726 ($\Delta = 31$)	1404 (1399) 1755, 1725 ($\Delta = 30$)	1376 (1371)	1390

Syntheses of Co(II), Mn(II), Cd(II), Zn(II), and Ni(II) complexes

Cobalt, cadmium, and zinc complexes were synthesized by following the procedures reported in the literature [1, 22].



Scheme 3 The proposed coordination environments of (**2**) (**a**) and (**5**) (**b**) complexes

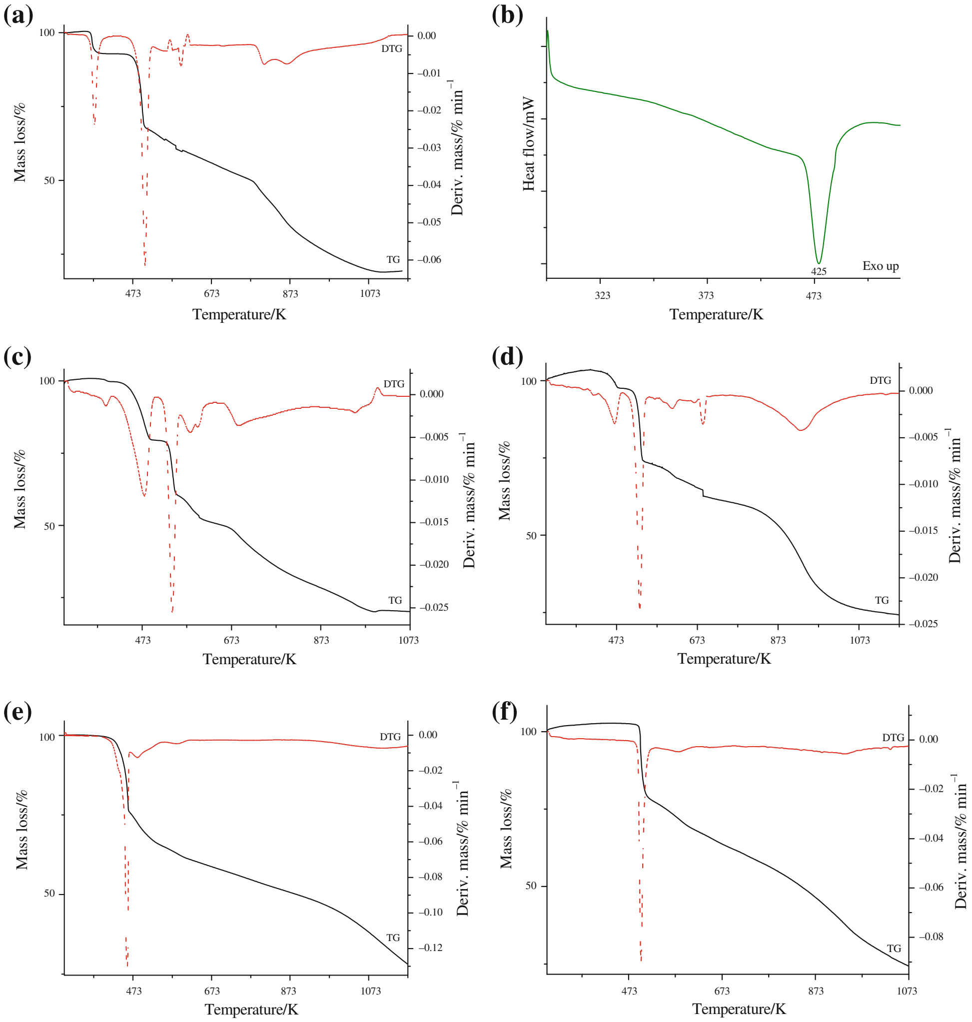
Preparation of manganese complex (**2**)

A water solution of $Mn(NO_3)_2{\cdot}4H_2O$ (0.1255 g, 0.5 mmol) was added dropwise to a solution of 4-CHO-5-MeIm (0.1102 g, 1 mmol) in 20 mL of pure MeOH. The molar ratio Mn:L was 1:2. The solution was stirred for 3 h at room temperature and left to crystallize. After 3 weeks, colorless precipitate was obtained. The crystals were filtered, washed with 20 mL of *i*-PrOH, and dried under vacuum. The product was collected in 44% yield.

Preparation of nickel complex (**5**)

The examined complex was obtained from the same mixture of solvent. 20 mL of the solution containing $Ni(NO_3)_2{\cdot}6H_2O$ (0.0727 g, 0.25 mmol) was gradually added with constant stirring to a 20 mL solution of 4-CHO-5-MeIm (0.0551 g, 0.5 mmol). The molar ratio Ni:L was 1:2. It was left to stand at RT for a few days and the resulting fine blue

Fig. 1 TG/DTG curves of complexes (**1**) (**a**), (**2**) (**c**), (**3**) (**d**), (**4**) (**e**) in N_2, and (**5**) (**f**) in argon atmosphere and DSC curves of complex (**1**) (**b**)



crystals were filtered off, and washed. The complex was dried in vacuum box. Yield 46%.

Preparation of cobalt complex (**1**)

To a solution of 4-CHO-5-MeIm (0.111 g, 1.0 mmol) in *i*-PrOH (20 mL), a solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.073 g, 0.25 mmol) in the same solvent was added. The mixture was stirred at RT for 1 h. The molar ratio Co:L was 1:4. After evaporation of half the solution (about 4–5 days), orange-pink plates were collected by filtration and dried in vacuum box. Yield 32%.

Preparation of cadmium complex (**3**)

4-CHO-5-MeIm (0.221 g, 2.0 mmol) dissolved in 20 mL of analytically pure EtOH was stirred with $Cd(NO_3)_2 \cdot 4H_2O$ (0.155 g, 0.5 mmol) dissolved in 20 mL of the same solvent. The molar Cd:L ratio was 1:2. The solution was set aside to crystallize at −2 °C. After 2 weeks, colorless crystals were obtained. The product was separated by filtration, washed with 30 mL of *i*-PrOH, and dried under vacuum conditions. The compound was collected in 59% yield.

Preparation of zinc complex (**4**)

A sample of 4-CHO-5-MeIm (0.331 g, 3 mmol) dissolved in mixture of analytically pure MeOH (12 mL) and redistilled water (12 mL) was added to the same solvents (24 mL) containing $Zn(NO_3)_2 \cdot 6H_2O$ (0.149 g, 0.5 mmol). The molar ratio Zn:L was 1:6. The solution was stirred for 7 h and left to crystallize at RT. After 2 weeks, colorless crystals of the complex were collected. The compound was filtered off and dried in vacuum box. Yield 38%.

Elemental analysis data of the obtained complexes considered in this study were summarized as Table 1.

Results and discussion

IR and Raman spectra

The most important spectra bands of the ligand and the Co(II), Mn(II), Cd(II), Zn(II), and Ni(II) complexes with their probable assignments are listed in Table 2. Unfortunately, the Raman data for Ni(II) complex was not included in Table 2 because a sample of Ni(II) compound was damaged during the experiment.

The free ligand display an imidazole C=N stretching frequencies at 1455 and 1439 cm^{-1}. The IR stretching frequency of the carbonyl group ($\nu_{C=O}$) is found at 1665 cm^{-1}. In the IR spectra of (**1**), the medium and broad bands in the range 3500–3350 cm^{-1} are assigned as the characteristic peak of ν_{OH} stretching vibrations from the coordinated water molecules. Upon coordination of 4-CHO-5-MeIm with examined transition metal ions,

Table 3 Thermoanalytical results (TG and DTG) of 4-CHO-5–MeIm complexes

Complex	Step	TG range/K	Mass loss/%		Assignment	Final product
			Found	Calcd.		
$[CoL_2(H_2O)_2](NO_3)_2$ (**1**)	I	353–403	7.42	8.21	2 H_2O	CoO
	II	403–523	25.84	28.24	2 nitrates	
	III	523–1163	48.17	46.51	1.85 L	
	Σ		81.43	82.96		
$[MnL_2(NO_3)_2]$ (**2**)	I	363–503	21.63	20.97	0.76 L	MnO
	II	503–633	28.97	25.44	NO, NO_2, 0.24 L	
	III	633–993	31.12	35.92	O_2, L	
	Σ		81.72	82.33		
$[CdL_2(NO_3)_2]$ (**3**)	I	393–483	5.79	6.59	0.27 L	Cd
	II	483–558	24.37	27.16	2 nitrates	
	III	558–1163	43.09	41.64	1.73 L	
	Σ		73.25	75.39		
$[ZnL_4](NO_3)_2$ (**4**)	I	373–563	29.46	29.24	0.55 L, 2 nitrates	ZnN_4
	II	563–1173	49.24	51.48	2.94 L	
	Σ		78.70	80.72		
$[NiL_3](NO_3)_2$ (**5**)	I	358–533	24.72	24.17	2 nitrates	NiN_3
	II	533–623	9.58	8.79	0.41 L	
	III	623–1073	43.25	47.41	2.21 L	
	Σ		77.55	80.37		

Table 4 XRD pattern of final product and powder diffraction file no. 9–402

Measured pattern			9–402 CoO	
$2\theta/°$	d_{hkl}/Å	I_{int}/%	d_{hkl}/Å	I_{int}/%
36.86	2.438	70	2.457	90
42.58	2.123	100	2.132	100
61.78	1.501	60	1.506	80
73.98	1.281	50	1.285	50
	Unmatched		1.230	40
	Unmatched		1.065	30
	Unmatched		0.978	35
109.60	0.943	65	0.952	60

Table 5 XRD pattern of final product and powder diffraction file no. 7–230

Measured pattern			7–230 MnO	
$2\theta/°$	d_{hkl}/Å	I_{int}/%	d_{hkl}/Å	I_{int}/%
35.00	2.564	55	2.571	60
40.70	2.217	100	2.222	100
58.73	1.572	65	1.570	60

except for Zn^{2+}, the stretching frequency of the carbonyl group ($\nu_{C=O}$) is shifted to lower wavenumber (from 1660 to 1574 cm^{-1}) compared to the free ligand. This indicates that –C=O [33] is coordinated to the central atoms, and proves presence of expected M–O coordination bonds. In all the complexes, the absorption due to $\nu_{C=N}$ appears between 1476 and 1434 cm^{-1}, compared to the 4-CHO-5-MeIm, indicating that coordination of the ligand is through the pyridine nitrogen (Nτ) atom of heteroaromatic ring. The strong new bands in the region 1420–1350 cm^{-1} can be assigned to νNO_3^- of nitrate ion [33]. This indicates presence of coordinated and non-coordinated anions in complexes. According to Lever [34], the NO_3^- in the manganese(II) and cadmium(II) complexes would be coordinated as bidentate because the separation of two peaks in the 1800–1700 cm^{-1} region are 30 and 31 cm^{-1}, respectively. In the complexes (**1**), (**4**), and (**5**), additional band at 1365, 1376, and 1390 cm^{-1} attributed to the existence of nitrates as counter ions. It is noteworthy that the structural data supported by IR data reveals stabilization of tautomer (**2**) of the ligand as the only form able to participate in the formation of a five-membered (Nτ),O chelate ring with Co(II), Mn(II), Cd(II), and Ni(II) giving CoN_2O_4, MnN_2O_6, CdN_2O_6, and NiN_3O_3 chromophore, respectively.

Based on the elemental analysis, spectroscopic IR, and comparative analysis, it was possible to suggest structural model for the $[MnL_2(NO_3)_2]$ and $[NiL_3](NO_3)_2$ compounds. The proposed structures are shown in Scheme 3.

Thermal studies

Figure 1a–f shows the results of the thermogravimetric analyses performed on Co(II), Mn(II), Cd(II), Zn(II), and Ni(II) compounds. The data characteristic of the thermal decomposition of the complexes are collected in Table 3.

The TG, DTG curves of $[CoL_2(H_2O)_2](NO_3)_2$ in nitrogen atmosphere are displayed in Fig. 1a. The TG curve of (**1**) exhibits three main distinct decomposition steps. The two molecules of water are released in temperature range 353–403 K (7.42%) [35]. At the DSC curve (Fig. 1b), an endothermic effects are observed. In the second step (403–523 K), complex (**1**) loses two nitrates (25.84%). The successive mass loss from 523 to 1163 K may be attributed to the gradual elimination of loss of two ligands with fragments of ligand donor atom-containing. The oxide CoO forms in this step [35–37]. The final residue was confirmed from their XRD patterns (Table 4) [38].

The TG and DTG curves of complex $[MnL_2(NO_3)_2]$ are shown in Fig. 1c. The TG curve exhibits three main distinct decomposition steps. In the first stage, the mass loss is 21.63% due to release of two methyl groups with fragments of imidazole rings. The second step corresponds to the loss of the next fragment of two imidazole rings and NO, NO_2 (from nitrate anions) with mass loss 28.97% (calculated 25.44%). A further increase in temperature (633–993 K) causes rupture of the part of ligand containing N- and O-donor atoms and O_2 molecule (from coordinated nitrate ions). The total mass loss occurring up to 1,073 K is in agreement with the formation of MnO as a final residue (observed 18.28%, calculated 17.67%) [39, 40]. The final product was confirmed from their XRD patterns (Table 5) [41].

The sample of $[CdL_2(NO_3)_2]$ decomposes in three stages in the temperature range 303–1273 K (Fig. 1d). The first

Table 6 Relevant crystalographic and thermal data for complexes of Co(II), Cd(II), and Zn(II)

Complex	M–N	Temp. range of last stage/K	M–O/M···O/Å	Temp. range of last stage/K
$[Co(L)_2(H_2O)_2](NO_3)_2$ (**1**)	2.103(2), 2.085(2)	523–1163	2.186(2), 2.189(2)	523–1163
$[Cd(L)_2(NO_3)_2]$ (**3**)	2.2521(2), 2.2616(2)	558–1163	2.5426(2), 2.6121(2)	558–1163
$[Zn(L)_4](NO_3)_2$ (**4**)	2.022(3)	563–1173	3.065(3)	

step begins at 393 K and is attributed to the release of two methyl group of imidazole rings. The second mass loss corresponds to nitrates (observed 24.37%, calculated 27.16%). The final process is accompanied by the decomposition of aromatic rings with donor atoms connected with central ion. Further heating gives Cd (observed 26.75%, calculated 24.61%) as the final product.

The thermal decomposition behavior of zinc complex (Fig. 1e) is quite different from those of the examined compounds. As for $[ZnL_4](NO_3)_2$, no mass loss was observed below 363 K. 29.46% mass loss (TG) and intense peak (DTG) are observed in the first stage (calculated 29.24%) which is connected with elimination of two methyl groups and nitrates. The last stage is described by big mass loss of 49.24% (calculated 51.48%) and is accompanied by the defragmentation of four imidazole rings inclusive O-donor atoms. A residue of ZnN_4 (observed 21.3%, calculated 19.28%) remained.

The TG, DTG curves of $[NiL_3](NO_3)_2$ in argon atmosphere are displayed in Fig 1f. The TG curve of (**5**) exhibits three main distinct decomposition steps. The nitrates are released in temperature range 258–533 K (24.72%). In the second step, complex (**5**) loses 3 $-CH_3$ groups (9.58%). Elimination of next fragments of ligand donor atom-containing up to 1073 K takes place in the last stage (43.25%). The NiN_3 forms in this step as a result of decomposition process (22.45%).

The thermal data correlate very well with the molecular structure of Co(II), Cd(II), and Zn(II) complexes (Table 6). In Co(II), Mn(II), and Cd(II) compounds, the fragments of N-donor atom-containing ligands decompose in the last stages, contrary to Zn(II) and Ni(II) compounds, in which metal ion surrounded by N atoms remains until the end. The course of pyrolysis and molecular structure of the complexes lead to the same conclusion about the strength of metal–ligand bonds.

Magnetic properties

The room temperature magnetic moments of powdered samples of (**1**), (**2**), and (**5**) complexes are 4.53, 5.79, and 2.94 BM, respectively. Calculated values of μ_{eff} were close to that expected for uncoupled seven (**1**) and five (**2**) independent spins ($S = 7/2$, $S = 5/2$) of Co(II) and Mn(II). The value of magnetic moment of the (**5**) compound is typical for octahedral nickel(II) complexes.

Conclusions

- To compare thermal stability of Co(II), Zn(II), and Cd(II) complexes with 4-CHO-5-MeIm, the two complexes of formula $[MnL_2(NO_3)_2]$ and $[NiL_3](NO_3)_2$ have been prepared and structurally characterized. Elemental analysis and IR studies have confirmed a bidentate fashion of coordination of the ligand to Mn(II) and Ni(II) ions. Each of organic molecule is bound to the metallic centrum through the nitrogen (of imidazole ring) and oxygen (of carbonyl group) atom and forms five-membered chelate ring. IR spectra indicate that there are different coordination modes of the nitrate anions in compounds: non-coordinated (as counter ion in Ni(II) complex) and coordinated (bidentate in Mn(II) complex).
- The decomposition process of the studied ligand complexes in nitrogen (Co(II), Mn(II), Cd(II), and Zn(II) complexes) and argon (Ni(II) complex) atmosphere proceeds in three main stages, except Zn(II) complex (two stages of decomposition), in temperature range 353–1163 K. The final products of decomposition process are CoO, MnO, Cd, ZnN_4, NiN_3. The hydrated complex of Co(II) loses two molecules of coordination water in one step, which is connected with strong endothermic effect. The DSC data correlates very well with the X-ray data characterizing coordination of H_2O molecules. Peak at 425 K indicates that water molecules are engaged to a lot of hydrogen interactions [1]. In addition, because of the fact that our aim was to gain information on the structural dependence of the thermal properties within the investigated series, we have to admit that there are different coordination modes of the NO_3^- ions in complexes: non-coordinated (behaving as counter ion in the (**1**), (**4**), and (**5**) complexes) and coordinated (bidentate in the (**2**) and (**3**) compounds). Thus, temperature ranges of its decompositions are observed: below 533 K and above 533 K, respectively. It is much lower in comparison with other trace metal complexes found in the literature [27, 42]. The thermal data correlate very well with the molecular structure of Co(II), Cd(II), and Zn(II) complexes. In Co(II), Mn(II), and Cd(II) complexes, the fragments of N-donor atom-containing ligands decompose in the last stages, contrary to Zn(II) and Ni(II) compounds, in which metal ion surrounded by N atoms remains until the end. The course of pyrolysis and molecular structure of the complexes lead to the same conclusion about the strength of metal–ligand bonds.
- On the basis of the above results, it is concluded that the thermal stability of the studied compounds follows the order: (**1**) < (**5**) < (**2**) < (**3**) < (**4**).

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